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Molecular Rectangles Based on Rhenium(I) Coordination Chemistry

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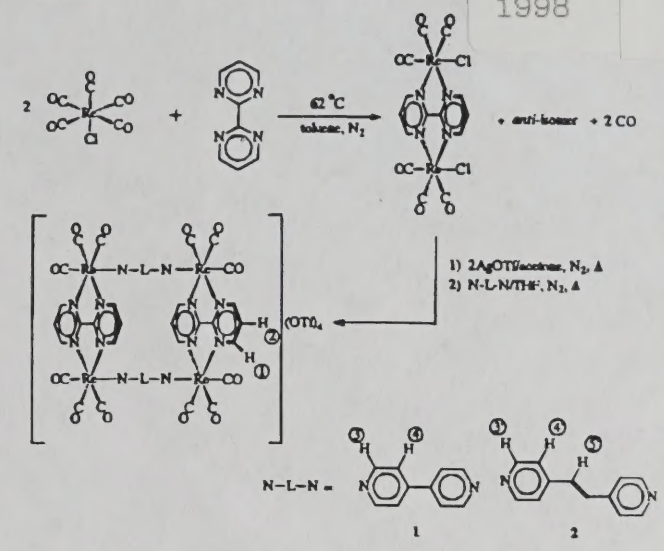
There has been substantial recent interest in the assembly of rigid inorganic and organometallic host species based on transition metal corners and difunctional organic ligand edges.[1−5] Most of these compounds are tetrametallic with a square geometry.[6] Several have now been shown to bind small molecules,[1a−c,2,3a] and some have been used as solution phase sensors.[3a,7] Because the cavities of the squares tend to align to form channels in the solid state,[2,3b] the compounds also are potentially useful in sieving and separations applications. Indeed, in initial electrochemical sieving studies involving redox active permeants, thin films of neutral rhenium-derived molecular squares have displayed size-selective permeant transport capabilities.[8] A compelling extension of the size-selective tetrametallic host chemistry would be the induction of significant guest shape selectivity. Toward this goal, we report the synthesis, characterization, and preliminary binding properties of two members of a new class of tetrametallic hosts featuring rectangular cavities.

Our earlier attempts to make a mixed-ligand tetrametallic cyclophane, of similar dimensions to the rectangular cyclophanes reported by Odell and co-workers[9] and by Geuder and co-workers[10] and derived from the original tetrarhenium squares (i.e., alternating 4,4′-bipyridyl and pyrazyl edges), gave only the square molecules, not rectangles. Some success in rectangle synthesis was achieved by using a two-step process to synthesize first a relatively robust rhenium−thiolate dimeric edge and then the molecular rectangle.[11] The cavity height (~3.8 Å) is insufficient, however, to allow the molecule to function as a host. Nevertheless, by building upon that strategy we have now been able to synthesize molecular rectangles by first creating a stabilized bimetallic edge by using a difunctional chelating bridge, 2,2′-bipyrimidine (bpym), and then adding difunctional pyridyl-based bridges (Scheme 1).

Scheme 1



Briefly, $[Cl(CO)_3Re]_2$bpym edges were formed in one step by an extension of Vogler's synthesis for the mononuclear complex $Cl(CO)_3Re$(bpym).[12] By heating 2 equiv of $Re(CO)_5Cl$ with 1 equiv of bpym in toluene for 4 h, collecting the red precipitate, and then recrystallizing in boiling acetone/diethyl ether, the pure product was obtained. Note, however, that a statistical mixture of syn- and anti-isomers, with respect to the orientation of the two chlorides, is almost certainly present. Removal of the chloro ligands was affected by refluxing the complex in acetone dried over molecular sieves with slightly greater than 2 equiv of AgOTf (OTf = trifluoromethanesulfonate). After removal of the AgCl precipitate by Celite on a glass frit and removal of solvent by rotary evaporation, the crude product was reacted with 1 equiv of 4,4′-bipyridine (4,4′-bpy) in refluxing tetrahydrofuran for 2 days. The molecular rectangle **1** precipitated with yields approaching 50%. In view of the presumably 1:1 ratio of syn- and anti-isomers of $[Cl(CO)_3Re]_2$bpym, 50% is the maximum yield expected. As suggested for many of the molecular squares,[1] precipitation evidently occurs when a cycle (rectangle) is completed. Thus, intermediate species remain in solution, presumably as solvento complexes, until all of their rhenium centers and all ligand nitrogen atoms are coordinated. Note that the anti-isomer alone cannot form cycles and thus should remain soluble until very high molecular weight species are formed. The cis-derived product was characterized by ^{1}H NMR, elemental analysis, mass spectrometry, UV−vis and FTIR absorption, and X-ray crystallography.[13,14] The synthetic scheme was extended to form a second molecular rectangle, **2**, containing planar 1,2-bispyridylethylene

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(13) The ^{1}H NMR spectrum appears as expected for **1** (DMSO-d_6): δ 7.47 (H1, d, J = 6.09 Hz, 8H), 8.34 (H2, d, J = 5.73 Hz, 8H), 8.50 (H4, t, J = 5.76 Hz, 4H), 9.98 (H3, d, J = 5.49 Hz, 8H). Elemental analysis for **1**: calculated C, 27.09; H, 1.72; N, 7.29; found C, 26.41; H, 1.45; N, 7.17. ES-MS: 2156.9 (*m/z* calculated M − $^-$OTf), 2157.1 (*m/z* observed). The IR absorption spectrum in acetone shows two bands in the carbonyl region: 2044 and 1954 cm^{-1}.

(14) Crystal data for **1**: monoclinic; space group $P2_1/n$ (No. 14), color: orange, a = 16.235(1) Å, b = 12.223(1) Å, c = 20.704(2) Å, β = 101.105-(1)°, V = 4031.5(9) Å^3, Z = 2, final R value of 0.083 for 7478 unique reflections, Goodness of Fit: 1.42.

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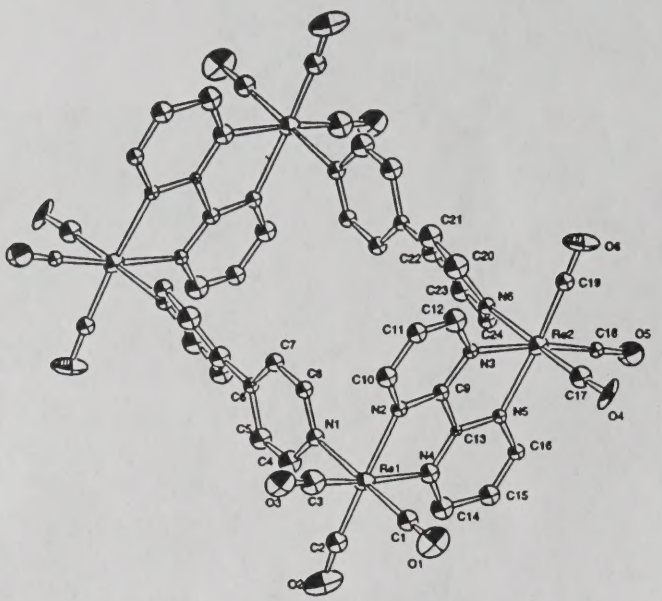

Figure 1. ORTEP of **1** with hydrogens excluded for clarity. The four counterions and four solvent molecules (acetone) are also excluded. The molecule sits on an inversion center which is located at the center of the cavity. Thermal ellipsoids are drawn to 50% probability.

(bpe) ligands as bridges. Synthesis of **2** was confirmed by ^{1}H NMR, elemental analysis, mass spectrometry, and UV−vis and FTIR absorption.[15] Attempts to synthesize a pyrazine-bridged rectangle were unsuccessful. **1** and **2** are highly soluble in polar organic solvents such as dimethyl sulfoxide (DMSO), acetonitrile, and acetone but have limited solubility in water.

X-ray quality crystals of **1** were grown by layering a solution of the rectangle in acetone with hexanes. The structure (Figure 1) shows a cavity with dimensions of 5.85 × 11.55 Å, as defined by the rhenium centers. The structure also shows that the 4,4′-bpy bridges are twisted ($\phi = 35°$), a feature presumably absent in the bpe-bridged analogue. The packing of the structure shows that the rectangles form channels, although they are offset so that a rectangle is not directly above the one below. (The organic rectangles of Odell et al. show similar offset packing.[9]) In addition, two triflate anions are seen within these channels, but not within the molecular cavity. The other two counterions are located outside of the channels. Four acetone molecules are also found in the structure, with two in the channels, but outside of the cavity, and two outside of the channels.

The electronic absorption spectrum for **1** is characterized by a solvatochromic band at 484 nm in DMSO (490 nm in H_2O, 450 nm in CH_3CN) and a solvent insensitive band at 322 nm. These are assigned as dπ (Re) to π^* (bpym) charge-transfer and aromatic ligand localized transitions, respectively. For **2** the corresponding bands are found at 476 nm (DMSO) and 330 nm.

Visible and UV excitation of **1** in CH_3CN at room temperature yielded no detectable luminescence. Notably, the parent compound, $[Cl(CO)_3Re]_2$bpym, is also nonluminescent,[12] a finding that has been rationalized on the basis of energy gap considerations.[16] Electrochemical interrogation of **1** by cyclic voltametery in acetonitrile yielded only irreversible waves for both the reduction and oxidation reactions.

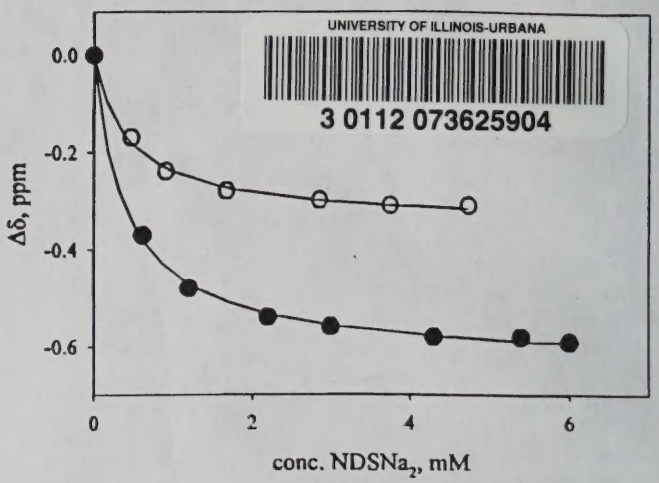

Figure 2. Change in chemical shift of ^{1}H 4 for **1** (○) and of ^{1}H 5′ for **2** (●) in DMSO as a function of added $NDSNa_2$. [host] ≈ 9 × 10^{-5} M. Lines shown are best fits based on 1:1 host/guest ratios. Fitting to a consecutive 1:2 binding scheme gave similar association constants.

Preliminary studies were undertaken to determine the affinity of **1** for a guest, 2,6-naphthalenedisulfonic acid, disodium salt ($NDSNa_2$, a planar aromatic species with aproximate length of 10 Å) in solution. Binding in DMSO-d_6 as solvent was monitored by following the change in chemical shift ($\Delta\delta$) of proton 4 (see Scheme 1 for the proton numbering scheme) by ^{1}H NMR (300 MHz Varian) and gave an association constant of 2.3 × 10^3 M^{-1} (Figure 2). The binding studies were conducted in DMSO-d_6 because the host was insufficiently soluble in D_2O to yield acceptable signals. Interestingly, attempts to use a 1:1 (v:v) mixture of DMSO-d_6 and D_2O as a solvent for **1** were unsuccessful because $NDSNa_2$ addition caused quantitative precipitation of **1**. Similar binding studies conducted using **2**—this time monitoring the $\Delta\delta$ of proton 5′ (Figure 2)—yielded an association constant of 2.4 × 10^3 M^{-1}. It should be noted that the binding clearly must include a favorable Coulombic component, in addition to any van der Waals components. In contrast, no binding of the roughly spherical tetraphenylborate anion (sodium salt) by **2** was detected in NMR studies. (**1** was not examined.)

In summary, a new set of tetracationic rectangular molecules has been synthesized using transition-metal corners. Preliminary studies have shown that both **1** and **2** bind a representative planar anionic guest molecule, albeit comparatively weakly. Our current efforts are focused on: (1) incorporation of dianionic chelating bridges so as to yield neutral rectangles and (2) use of alternative di- and trifunctional ligands to bridge the dirhenium edges, with the aim of inducing more useful binding and sensing properties.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, least squares planes, and anisotropic thermal parameters for **1** (14 pages print). An X-ray crystallographic file, in CIF format, for **1** is available through the Web only. See any current masthead page for ordering information and Web access instructions.

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(15) ^{1}H NMR spectrum for **2** (DMSO-d_6): δ 7.25 (H4′, d, J = 6.81 Hz, 8H), 7.36 (H5′, s, 4H), 8.20 (H3′, d, J = 6.30 Hz, 8H), 8.49 (H2, t, J = 5.94 Hz, 4H), 9.94 (H1, d, J = 5.70 Hz, 8H). Elemental analysis for **2**: calculated C, 28.52; H, 1.37; N, 7.13; found C, 28.61; H, 1.65; N, 7.10. ES-MS 2208.9 (*m/z* calculated M − $^-$OTf), 2209.1 (*m/z* observed). IR absorption spectrum (carbonyl region) 2043 and 1953 cm^{-1}.

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